

SPECTROSCOPIC ANALYSES OF FE AND WATER IN CLAYS. A MARTIAN SURFACE WEATHERING STUDY; J. L. Bishop, C. M. Pieters and J. O. Edwards, Brown University, L. M. Coyne, San Jose St. Univ. and S. Chang, NASA-ARC, Moffett Field, CA

Martian surface morphology suggests the presence of liquid H_2O on Mars in the past.¹ Visible and NIR reflectance spectra of the Martian surface include features which correspond to the crystal field transitions of iron², as well as features supporting the presence of ice and minerals containing structural OH and surface water.³ Clays have been associated with the Martian surface through reflectance spectroscopy and the Viking chemistry and biology experiments.^{4,5} We have initiated further spectroscopic studies of surface iron and water and structural OH in clays in order to determine what remotely obtained spectra can indicate about the presence of clays on Mars based on a clearer understanding of the factors influencing the spectral features. Vibrational spectroscopy of minerals has involved in the past either the diagnostic Near-Infrared (NIR) or the fundamental Mid-IR regions. Current technology allows us to better correlate the low frequency fundamental stretching and bending vibrations of O-H bonds with the diagnostic water NIR overtone and combination bands used in mineral characterization and identification.

The spectral features in clays near 1.4, 1.9 and 2.2 μm are comprised of multiple overlapping peaks which vary as a function of octahedral cation and bond strength of structural OH and adsorbed water molecules.^{6,7,8} Therefore, understanding these vibrations in minerals requires understanding the chemical environment of water molecules and hydroxyl groups in minerals. Extensive H-bonding in water lowers the vibrational energy of the stretching and bending frequencies. Bound water induces broadening of the absorption features as the vibrational energies become widely distributed. The interlayer cations also affect these fundamental vibrations by interacting with the water molecules (e.g. forming cation-water clusters⁹) and by migrating into the hexagonal hole of the silicate layer.^{7,10} (for example) In order to more accurately understand the effect of clay composition on the shape of the 1.4, 1.9 and 2.2 μm features, we are examining a series of montmorillonite samples prepared with varying quantities of exchangeable iron and water.

SWy-1 montmorillonite was obtained from the Clay Mineral Society, Source Clays Repository as a starting material. The naturally present Ca and Na interlayer cations were then exchanged chemically with varying amounts of Fe, Ca, Na and H according to the Banin method.² Due to the swelling properties of smectite clays the interlayer regions can accommodate exchange values above the normal 100% cation exchange capacity (CEC). The clays were dried through lyophilization, ground by hand and then sieved to < 125 μm particle size. X-Ray fluorescence analysis was performed to enable us to make quantitative correlations of the composition with spectral features. Spectra were measured using the RELAB (reflectance experiment laboratory) at Brown University (0.3 - 3.6 μm) and a Nicolet 740 FTIR (the 1 - 5 μm range was measured using a PbSe detector and the 2 - 25 μm range using a TGS detector). Nicolet spectra were measured against KBr and the sample chamber can be purged with water-free air. RELAB spectra were measured using a halon standard and were obtained under ambient atmospheric humidity.

Initial spectra have been obtained with the Nicolet and the band shape and position of spectral features in the NIR and Mid-IR overlap regions correlate well (Fig.1). A spectrum of the 100% Fe-clay (Fig.1) shows the stretching (ν) and bending (δ) vibrations for structural OH and bound water¹¹: ν_{OH} (2.75 μm), ν_w (~3 μm), δ_w (~6 μm), δ_{OH} (11-12 μm) and the NIR overtone and combination water bands⁶: $2\nu_{OH}$ (1.41 μm), $\nu'_w + 2\delta_w$ (1.41 μm), $\nu_w + 2\delta_w$ (1.45 μm), $\nu'_w + \delta_w$ (1.91 μm), $\nu_w + \delta_w$ (1.97 μm), $\nu_{OH} + \delta_{AlOH}$ (2.2 μm). (ν'_w indicates the stretching vibration of residual interlayer water molecules and has an energy slightly less than ν_{OH}). Fig.2 shows NIR spectra of 300% Fe-exchanged montmorillonite obtained using a) Nicolet, purged, b) Nicolet, unpurged and c) RELAB. Slight increases in moisture content from a) to c) exemplify the differences in character of the water represented in the peaks and shoulders of the NIR features. For example, the growth of the 1.9 μm peak relative to the 1.4 μm peak implies that the 1.9 μm peak has more bound water

character. Fig.3 shows significant variability in the shape of ν_w (bound water stretching vibration) as a function of interlayer cation for the exchanged clays (spectra measured under purged conditions with the Nicolet FTIR): the sharper portion of the peak represents structural OH and residual water, while the broader portion near $3 \mu\text{m}$ represents molecular water with significant H-bonding. These spectra show the strong effects that interlayer cations have on the stretching vibrations of interlayer water. Shown in Fig.4 are the crystal field Fe transitions near $0.9 \mu\text{m}$ and the diagnostic NIR features of a) 100 % Fe-clay, b) 200 % Fe-clay, c) 300 % Fe-clay and d) 600 % Fe-clay (spectra measured with the RELAB spectrometer). The 1.4 , 1.9 and $2.2 \mu\text{m}$ features are all suppressed in the 600 % Fe-clay relative to the others. The larger amount of Fe in this sample was verified through XRF and is shown spectroscopically by the deep Fe crystal field band. A similar reversal in band intensity in the NIR water features has been observed in other highly exchanged Fe-montmorillonite,¹² which suggests a complex Fe-water relationship in Fe-rich clays. Our initial spectra show variability in the fundamental stretching and bending vibrations of surface water as a function of surface cation. More detailed analyses will explore the effects of these cations on the NIR combination and overtone bands.

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